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6. AUTHOR(S)
Z. A. Munir

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
University of California, Davis, CA 95616

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13. ABSTRACT (Maximum 200 words)

The broad objective of the completed work was to investigate the effect of mechanical and electric field activation on the synthesis and properties of materials, with special emphasis on nanostructured hard materials. We have investigated several aspects of this, including: (a) Synthesis and Microstructural Evolution under Field Application, (b) Synthesis of Bulk Nanostructured Materials by Mechanical and Field Activation, (c) Investigations on FGM Formation and Properties, (d) Investigations on the Field Activated Synthesis Complex and Hard Materials, (e) Modeling Studies, (f) Microalloying, (g) Field Activated Consolidation and Crystallization of Bulk Metallic Glasses, and (h) Synthesis of Ultra-Hard Boride Phases. Brief descriptions of the accomplishments in each of these thrusts are provided, with details given in the cited publications listed at the end of this report.

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SUMMARY OF RESULTS

(a) Synthesis and Microstructural Evolution under Field Application

The focus of this aspect of our work is to understand the effect of the field on the microstructural development during synthesis. We investigated the influence of the magnitude of the field on particle size of TiC in the TiNi matrix in TiNi-TiC composites (Graeve and Munir, *J. Alloys Compounds*, **340**, 79-87, 2002). The average particle size increased by at least a factor of two when the field was increased from zero to 5 $V.cm^{-1}$. Although higher temperatures and wave velocities result in steeper temperature gradients and thus an anticipation of shorter residence time at the highest temperatures, the presence of a liquid phase has apparently a more direct effect on TiC particle growth.

To assess the validity of the above interpretation, we conducted research on a system where no liquid forms during the SHS process. For this we have investigated the formation of TaC, a process where the adiabatic temperature is lower than the melting point of reactants and product (Graeve and Munir, *J. Mater. Res.*, **17**, 609-613, 2002). The product was nanocrstalline TaC (30-55 nm) for fields in the range 8.54-16.39 $V.cm^{-1}$ and the size showed little dependence on field strength. However, the size increased significantly at field higher than 16.39 $V.cm^{-1}$. It was shown that at this field the combustion temperature corresponded to the melting point of Ta. Furthermore, the composition of the product had a dependence on the magnitude of the applied field. At low fields, the product contained Ta_2C, but becomes pure TaC when the filed strength is relatively high.

We have also investigated the effect of a current in the SPS process on the structural evolution during the formation of zirconia-toughened mullite composite from zircon/alumina powder mixtures (Yu, et al., Proc. First Intern. Sympos. On Spark Plasma Sintering, pp. 55-67, 2001; Khor et al., *Mater. Sci. Eng.*, **A339**, 286-296, 2003). It was shown that the process begins, at lower temperatures, with the decomposition of zircon to form nanocrystallites of t-ZrO_2 embedded in an amorphous silica matrix. Mullite then forms at higher temperatures as part of a homogeneous composite with m-ZrO_2. The process of formation of the composite was related to phase evolution and the concomitant increase in hardness, Young's modulus, and fracture toughness. A fracture toughness of 11.2 $MPa.m^{1/2}$ was obtained for this composite.

We have also investigated the effect of mechanical activation and associated phase transformations on the kinetics of subsequent SPS synthesis of $MoSi_2$ (Sannia, et al., *Mater. Sci. Eng.*, **A345**, 270-277, 2003). Milling produced significant changes in the dispersion and crystallite size of the reactants initially, and resulted in the partial formation of the product in both the low-temperature (alpha) and high-temperature (beta) modifications when longer milling times were employed. Subsequent field-activated synthesis resulted in the formation of alpha-$MoSi_2$ only. The initiation of the synthesis reaction required a threshold power level (equivalent to the level of the current), with the threshold decreasing with increased milling time. However, the initiation time increased when milling resulted in the formation of a significant amount the product phase, with the increase being markedly significant at low power levels.

(b) Synthesis of Bulk Nanostructured Materials by Mechanical and Field Activation

As pointed out above, we have succeeded in synthesizing bulk dense nanostructured materials including ceramics, intermetallics, and composites. This represents an important practical accomplishment, since previous efforts to consolidate nanopowders have generally not been successful. Our accomplishment in this regard has resulted in two patents: a US Patent (Munir, et al. US Patent No. 6,200,515, March 13, 2001) and a recently approved International Patent (Munir et al., International Patent Application, allowed March 24, 2005 (Europe).

The formation of dense nanometric TiB_2-TiC composites from ball milled elemental reactants was investigated (Lee et al., *Mater. Sci. Eng.*, **325**, 221-227, 2002). Elemental powders (Ti, C and B) were milled to (a) produce nanometric powders without product formation or (b) to effect a reaction during milling to produce nanostructured TiB_2 and TiC. The products of these two mechanical activations were reacted/consolidated or only consolidated under the influence of a high current and a uniaxial pressure. Dense (up to 98.6%), bulk nanocomposites were formed. The effect of prior milling on the crystallite sizes of the composite components was studied. The crystallite sizes of TiB_2 and TiC in the dense composite formed from powders milled for 10 h were 71.4 and 62.5 nm, respectively. The microhardness of this composite was 20.6 GPa.

We have also investigated the synthesis of nanostructured $NbAl_3$ using this approach (Gauthier, et al., Intermetallics, 9, 571-580, 2001). Nb+3Al elemental powders were co-milled for a short time in a specially designed planetary ball mill to obtain nanoscale- distributed reactants but to avoid the formation of product phases. These were then subjected to high AC currents (1500-1650 A) and uniaxial pressures (56-84 MPa). Under these conditions, a reaction is initiated by field activation and completed within a short period of tithe (3-6 min). The end-product relative density ranged from 85 to 96% and the $NbAl_3$ crystallite size, determined by XRD line-broadening analysis using the Langford method, was in the range of 57-150 um.

We have also investigated the synthesis of dense nanometric composites of TiN-TiB_2 by mechanical and field activation from powder mixtures of Ti, BN, and B (Lee et al. *J. Amer. Ceram. Soc.*, **84**, 1209-1216, 2001). Powders were either milled to reduce crystallite size but to avoid initiating a reaction or were milled until they reacted partially. These were subsequently reacted/densified in a spark plasma synthesis (SPS) apparatus. The products were composites with equimolar nitride and boride components with relative densities ranging from 90.1% to 97.2%. Crystallite size analyses using the XRD treatments of Williamson-Hall and Halder-Wagner gave crystallite sizes for the TiN and TiB_2 components in the range 38.5-62.5 and 31.2-58.8 nm, respectively. Vickers microhardness measurements (at 2 N force) on the dense samples gave values ranging from 14.8 to 21.8 GPa and fracture toughness determinations (at 20 N) resulted in values ranging from 3.32 to 6.50 MPa $.m^{1/2}$.

The effect of mechanical and field activation on the synthesis of dense nanometric $MoSi_2$ was investigated (Orru et al., *J. Mater. Res.*, **16**, 1439-1448, 2001). Powders of Mo and Si, milled separately or co-milled in a planetary ball mill, were reacted in a spark plasma synthesis (SPS) apparatus under different electric current conditions. Milled powders reacted faster and required less current than unmilled powders. Mixtures of powders which were milled separately (to nanometric size) reacted in the SPS to produce micrometric α–$MoSi_2$. Similar results were obtained for samples co-milled to produce nanometric reactants which did not contain detectable amounts of the product phase. When products form during milling, they contain both the α and β modifications of $MoSi_2$. The product after the SPS reaction was nanometric $MoSi_2$ with a crystallite size of 140 nm.

In a more recent collaborative work, we have been successful in densifying nano-powders of SiC using the SPS method (Ohyanagi, et al., Proceedings of the International Conference on Materials and Technology (CIMTEC 2002), Florence, Italy, July 15-18, 2002. pp. 175-182; T. Yamamoto, et al., *J. Amer. Ceram. Soc.*, **87**,1436-1441, 2004). Our results show that structural defects (stacking faults) play a major role in the densification process. We have conducted a similar investigation on B_4C since it also has structural defects (twins) and have reported these results in two papers (U. Anselmi-Tamburini, et al. *J. Amer. Ceram. Soc.,* in press, 2005; U. Anselmi-Tamburini, et al., *Chem. Mater.*, **16,** 4347-4351 , 2004).

(c) Investigations on FGM Formation and Properties

The formation of dense, layered, single- and graded-composition composites of $MoSi_2$ and SiC from elemental powders in one step was investigated using the field-activated pressure-assisted combustion method (Carrillo-Heian, et al., *J. Amer. Ceram. Soc.*, **84**, 962-968, 2001). Compositions ranging from 100% $MoSi_2$ to 100% SiC were synthesized, with relative densities ranging from 99% to 76%, respectively, X-ray diffraction results indicated the formation of pure phases when the concentration of $MoSi_2$ was high and the appearance of a ternary phase, $Mo_{4.8}Si_3\ C_{0.6}$, when the concentration of SiC was high. Electron microprobe analysis results showed the formation of stoichiometric and uniformly distributed phases. A layer-to-layer variation in composition of 10 mol% was sufficient to prevent thermal cracking during formation of the functionally graded materials.

We have also modeled the SPS process to provide an understanding of the mechanism of phase formation in the FGM system $MoSi_2$/SiC as an example (Heian and Munir, *Ceram. Trans.* **135**, 61-71, 2002). With a continuum model for heat transfer and electric field we found that large samples reacted in a wave mode while in smaller samples, the reaction was of a volume mode in each FGM layer. In all cases, the phase $MoSi_2$ formed before SiC. We have also investigated the effect of electrical conductivity on the process. The mode of reactions has implications with respect to microstructure due to differences in temperature gradients.

(d) Investigations on the Field Activated Synthesis Complex and Hard Materials

In a previous work we demonstrated a novel technique for the formation of *in situ* fiber-like precipitates in refractory boride solid solution matrices. In the more recent work we have investigated the formation of TiB_2-WB_2 solid solutions by induction field synthesis. Since the precipitation of the desired phase is kinetically slow, we have investigated the effect of additives of Ni and Co on this process. With these additives the decomposition was significantly enhanced (6 min as opposed to several hours without the field).

Solid solutions of titanium diboride-tungsten diboride (TiB_2-WB_2) were synthesized by induction-field-activated combustion synthesis (IFACS) using elemental reactants (Shibuya, et al., *J. Amer. Ceram. Soc.*, **86**, 706-710, 2003). In sharp contrast to conventional methods, solid solutions could be formed by the IFACS method within a very short time, about 2 min. Solutions with compositions ranging from 40-60 mol% WB_2 were synthesized with a stoichiometric ratio (Ti + W)/B = 1/2. The dependence of the lattice constants of the resulting solid solutions on composition was determined. The "a" parameter decreased only slightly with an increase in the WB_2 content, whereas the "c" parameter exhibited a significant decrease over the range 40-60 mol% WB_2. Solid-solution powders formed by the IFACS method were subsequently sintered in a spark plasma sintering (SPS) apparatus.

After 10 min at 1800°C, the samples densified to relative density 86%. XRD analysis showed the presence of only the solid-solution phase.

Solid solutions of TiB_2-WB_2 were densified and annealed simultaneously to cause the decomposition into the phases $(Ti,W)B_2$ and $(W,Ti)_2$ (Shibuya, et al., *J. Amer. Ceram. Soc.*, **86**, 354-356, 2003). Ni and Co were added to solid solutions formed by induction field activated combustion synthesis. The presence of these metals as additives markedly enhanced the kinetics of the subsequent decomposition process. With these additives, decomposition to the two phases occurred within minutes (6 min) in contrast to hours when the solutions did not include the additives. The phases resulting from decomposition, $(Ti,W)B_2$ and $(W,Ti)B_2$, were identified by X-ray to have the hexagonal AlB, and W_2B_5 structures, respectively. The precipitated phase, $(W,Ti)B_2$, occurred as elongated grains with aspect ratios of as high as about 10 in samples containing Ni as the additive.

Composites of TiN/TiB_2 were synthesized by a combustion process of BN, Ti in a nitrogen atmosphere (Shibuya, et al., *J. Amer. Ceram. Soc.*, **85**, 2965-2970, 2002). The effect of the BN/Ti ratio and the nitrogen gas pressure on the synthesis of these composites was investigated. Dense TiN/TiB_2 composites with relatively high hardness and toughness were fabricated by combustion synthesis from Ti and BN under a nitrogen pressure of 4.0 MPa. The Vickers microhardness of the products obtained from reactants with a BN/Ti mole ratio of 0.11 increased with an increase in nitrogen pressure and had a maximum value of about 25 GPa. Fracture toughness, K_{IC}, of the products increased from 3.1 to 5.9 $MPa.m^{1/2}$ as the BN/Ti ratio increased from 0.11 to 0.20. However, products formed under nitrogen pressures higher than 6.0 MPa exhibited circumferential macrocracks due to thermal shock.

Dense WC-x vol% Co composites, with WC grain size of about 1 μm, were synthesized by field-activated and pressure-assisted combustion synthesis (FAPACS) from elemental powders within several minutes (Park, et al., *J. Amer. Ceram. Soc.*, **85**, 2670-2677, 2002). Simultaneous synthesis and densification were accomplished under the combined effects of an electric field and mechanical pressure. The effect of cobalt content on the hardness, fracture toughness, and relative density of dense WC-x vol% cobalt composites was investigated. The relative density of the WC-cobalt composites increased with increased cobalt content. Under the application of a 60 MPa pressure and a 3000 A current, the final products had relatively high densities, 99.4%, for WC-20 vol% cobalt. The hardness of the WC-cobalt composites decreased with increased cobalt content, while the fracture toughness increased. The maximum fracture toughness and hardness values obtained were 9.4 $MPa.m^{1/2}$ for the WC-20 vol% cobalt composition and 2014 $kg.mm^{-2}$ for the WC-5 vol% cobalt composition.

The synthesis of WSi_2 and WSi_2-x vol.%Nb and WSi_2-y vol.%ZrO_2 composites with x, y= 0, 5, 7, 10, 12, 15, 17, 20 by field activated combustion was investigated (Shon, et al. , *J. Alloys Compounds*, **327**, 66-72, 2001). Self-propagating synthesis fronts can be initiated above minimum (threshold) values which depended on the amount of added Nb and ZrO_2. Reaction wave velocities had a direct dependence on the applied field and on the amount of the second phase. XRD results showed the presence of the WSi_2 phase in all systems with the additional phase of Nb or ZrO_2 for the composites.

The simultaneous synthesis and consolidation of WSi_2 and WSi_2-20 vol.% ZrO_2 from elemental powders of W, Si, and ZrO_2 additive was investigated (Shon, et al., *J.Alloys Compounds*, **322**, 120–126 (2001). The synthesis was carried out under the combined effect of an electric field and uniaxial pressure. The final density of the products increased nearly linearly with the applied pressure in the range 10 to 60 MPa. Highly dense WSi_2 and WSi_2-20 vol.% ZrO_2 with relative densities of up to 98.0% were produced with the application of a 60 MPa pressure and a 3000 A DC current. The percentages of the total shrinkage occurring before and during the

synthesis reaction were 17.5 and 82.5% for the case of WSi_2, and 25.8 and 74.2% for the case of WSi_2-20 vol.% ZrO_2, respectively. The respective Vickers microhardness values for these materials were 8.2 and 10.6 GPa. From indentation crack measurements, the fracture toughness values for WSi_2 and WSi_2-20 vol.% ZrO_2 were calculated to be 3.2 and 9.4 MPa $m^{1/2}$, respectively.

The synthesis of solid solutions of AIN-SiC was investigated through the combustion reaction between Si_3N_4, aluminum, and carbon powders and nitrogen gas at pressures ranging from 0.1 to 6.0 MPa (Kata, et al., *J. Amer. Ceram. Soc.* **84**, 726–732 (2001). The combustion reaction was initiated locally and then the wave front propagated spontaneously, passing through the cylindrical bed containing the loose powder. In the presence of Si_3N_4 as a reactant, it was feasible to synthesize solid solutions at an ambient pressure (0.1 MPa), The relationship between nitrogen pressure and full-width at half maximum of the (110) peak of the product showed that lower pressures produced more homogeneous solid solutions. Some aspects of formation of the AIN-SiC solid solutions were related to the influence of nitrogen pressure and reactant stoichiometry.

(e) Modeling Studies

This aspect of our work is aimed at providing a better understanding of the SPS process, a process that has gained considerable attention in recent years particularly in Japan and Europe (a second international symposium was held in conjunction with the IUMRS meeting in Yokohama and the 5th International Symposium on SPS is planned for the 6th Pac Rim Meeting in Hawaii in September, 2005). We have previously modeled the formation of single phases and demonstrated the change in the mode of combustion synthesis from volume combustion to wave combustion as the size of the sample increased. In the recent work we have modeled the formation of a composite ($MoSi_2$/SiC) by the SPS process (Carrillo-Heian, et al., *Acta Materialia,* **50**, 3331-3346, 2002).

The study was made to simulate the experimental process of spark plasma synthesis (SPS), which has been utilized previously to simultaneously synthesize and densify materials, including nanophases. The results show a temporal dependence for the formation of the two products. The dependence of the reaction wave dynamics on composition was also investigated. A transition from volume combustion, in which the reactants are converted instantly to the products throughout the entire sample, to a wavelike reaction, in which the conversion front traverses the sample in a finite time, is shown to depend on sample size and product. Conversion fronts traverse the sample as concentric waves propagating outward or inward depending on the composition of the composite and on the die conductivity. Since the two modes have distinctly different temperature profiles, they have an influence on the resulting microstructure. Thus the conditions under which a transition occurs are important parameters that influence the microstructural development of the product.

(f) Microalloying

Although this work has focused on $MoSi_2$, it has similar implications for other high temperature transition metal silicides. Their utilization is hampered, in part, by a high ductile-brittle transition temperature (DBT≈ 1000°C for $MoSi_2$). Theoretical calculations have shown that the incorporation of Mg into the Si sub-lattice has the most significant effect on the DBT. However, prior to our work, it was not possible to accomplish the goal of incorporating Mg. Through a combination of mechanical activation and field enhancement, we have succeeded in achieving this goal (Woolman et al., *Scripta Materialia.* **48**, 819-824, 2003; Woolman, et al. *J. Mater. Sci.* **39**, 5037-5043 (2004). This work has resulted in a US patent (Munir et al., Patent No. 6,613,276, September 2, 2003).

(g) Field Activated Consolidation and Crystallization of Bulk Metallic Glasses

The effect of a dc current on the crystallization of Vit1A ($Zr_{42.6}Ti_{12.4}Cu_{11.25}Ni_{10}Be_{23.75}$) and PCNP ($Pd_{40}Cu_{30}Ni_{10}P_{20}$) metallic glasses was investigated. Samples were isothermally annealed with and without the current, at 623 and 577 K for the two glasses, respectively. Small-angle neutron scattering (SANS) analyses showed that in the absence of a current, the annealed Vit1A samples were amorphous, but the imposition of a current enhanced the crystallization process, increasing both the size and volume fraction of the crystallites. Similar general observations were seen for the PCNP glass. Differential scanning calorimetry patterns of Vit1A samples indicate a lower thermal stability of samples annealed with a current (T. B. Holland, et al., *J. Appl. Phys.*, **95**, 2896-2899, 2004). We also have applied for a US patent (Munir, et al., Patent Disclosure submitted, February 13, 2003).

(h) Synthesis of Ultra-Hard Boride Phases

High B-content borides, such as $AlMgB_{14}$, have been of interest for applications in thermoelectric devices and in armor. This phase was reported to have an exceptionally high hardness (32-35 GPa), approaching that of cubic BN (45-50 GPa). Previous attempt to synthesize this phase have not been successful in obtaining a high purity product. Our recent research has the aim to produce high purity, nanostructured $AlMgB_{14}$. The most likely source of impurity is oxygen contamination. Our preliminary work indicated that the purity of boron and the handling of the powders are two important considerations in this regard. With respect to the latter, we have developed a method of handling powders in a glove box that promises to decrease the oxygen level and hence the relative amount of the main contaminant, $Al_2Mg_4O_4$ spinel. Our initial results, conducted before the development of the new powder handling facility, I showed the presence of the spinel phase, although at a much lower level than previously reported. This work continues with two immediate objectives: (a) to minimize the level of impurity (spinel) and (b) to synthesize nanostructured $AlMgB_{14}$ through the combination of mechanical activation (high-energy milling) and filed activation (the SPS process).

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PUBLICATIONS OF WORK SUPPORTED BY THE GRANT

A. Publications in Peer Reviewed Journals

- Dense Layered $MoSi_2$/SiC Functionally Graded Composites Formed By Field Activated Synthesis, E.M. Carrillo-Heian, R.D. Carpenter, G.H. Paulino, J.C. Gibeling, and Z.A. Munir, *J. Amer. Ceram. Soc.*, **84**, 962–968 (2001).
- Synthesis of Dense TiB_2-TiN Nanocrystalline Composites Through Mechanical And Field Activation, J. W. Lee, Z. A. Munir, M. Shibuya, and M. Ohyanagi, *J. Amer. Ceram. Soc.*, 84, 1209–1216 (2001).
- Synthesis and Densification of Ceramic FGMs in One Step, E. M. Carrillo-Heian, J. C. Gibeling, Z. A. Munir, and G. H. Paulino, Proceedings of FGM 2000, *Ceramic Transactions*, vol. 114, 241-248 (2001).
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- Synthesis of Dense Nanometric $MoSi_2$ through Mechanical and Field Activation, R. Orru, J. Woolman, G. Cao, and Z. A. Munir, *J. Mater. Res.*, **16**, 1439–1448 (2001).
- Synthesis of Nanocrystalline $NbAl_3$ by Mechanical and Field Activation, V. Gauthier, F. Bernard, E. Gaffet, Z. A. Munir, and J. P. Larpin, *Intermetallics*, **9**, 571–580 (2001).
- Dense WSi_2 And WSi_2-20vol% ZrO_2 Composites Synthesized by Pressure-Assisted Field-Activated Combustion, J. Shon, D. H. Rho, H. C. Kim, and Z. A. Munir, *J. Alloys Compounds*, **322**, 120–126 (2001).
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- A Kinetic Model for the Field-Activated Synthesis of $MoSi_2$/SiC Composites: Simulation Of SPS Conditions, E. M. Carrillo-Heian, A. Feng, and Z. A. Munir, *Acta Materialia,* 50, 3331-3346 (2002).
- The Effect of an Electric Field on the Microstructural Development during Combustion Synthesis Of TiNi-TiC Composites, O. A. Graeve and Z. A. Munir, *J. Alloys Compounds*, 340, 79-87 (2002).
- Electric Field Enhanced Synthesis of Nanostructured Tantalum Carbide, O. A. Graeve and Z. A. Munir, *J. Mater. Res.*, 17, 609-603 (2002).
- Simultaneous Synthesis and Consolidation of Nanostructured $MoSi_2$ C. Gras, F. Bernard, F. Charlot, E. Gaffet, and Z. A. Munir, *J. Mater. Res.*, 17,542-549 (2002).
- One Step Synthesis of Dense WC-Co Hard Materials, C. D. Park, H. C. Kim, I. J. Shon, and Z. A. Munir, *J. Amer. Ceram. Soc.*, **85**, 2670-2677 (2002).
- Analysis of the Formation of FGM Structures via Combustion Synthesis, E. M. Heian and Z. A. Munir, *Ceram. Trans.*, vol. **135**, 61-71 (2002).

- Dense Nanocrystalline TiB_2-TiC Composites Formed by Field Activation from High-Energy Ball Milled Reactants, J. W. Lee, Z. A. Munir, and M. Ohyanagi, *Mater. Sci. Eng.*, **325**, 221-227 (2002).
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SCIENTIFIC PERSONNEL

The following individuals were *involved or collaborated* in some aspect of the research summarized in the papers listed above:

Z. A. Munir, Principal Investigator, Distinguished Professor of Materials Science and Dean Emeritus of the College of Engineering.
M. A. Khor, Associate Professor, Nanyang Technological University, Singapore.
M. R. Hill, Asistant Professor, Department of Mechanical and Aeronautical Engineering, UC Davis.
G. Paulino, former Assistant Professor, Department of Civil and Environmental Engineering, UC Davis.
J. C. Gibeling, Professor, Department of Chemical Engineering and Materials Science, UC Davis.
R. D. Carpenter, former PhD student, UC Davis.
O. A. Graeve, former PhD student, UC Davis (currently Assistant Professor, University of Nevada, Reno).
F. Bernard, Professor, University of Burgundy, France.
E. M. Heian, Former Postdoc, UC Davis
I. J. Shon, Professor, Chonbuk National University, Korea.
M. Ohyanagi, Professor, Riyukoku Unoversity, Japan.
R. Orru, Assistant Professor, University of Cagliari, Italy.
M. Sannia, former Postdoc, University of Cagliari, Italy.
G. Cao, Professor, University of Cagliari, Italy.
J. N. Woolman, former PhD student, UC Davis.
J. J. Petrovic, Senior Scientist, LANL.
T. B. Holland, PhD student, UC Davis
D. Roberts, MS student, UC Davis.

INVENTIONS AND PATENTS

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